Mechanical Properties and Durability of Advanced Environmental Barrier Coatings in Calcium-Magnesium-Alumino-Silicate Environments

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Abstract

Environmental barrier coatings are being developed and tested for use with SiC/SiC ceramic matrix composite (CMC) gas turbine engine components. Several oxide and silicate based compositions are being studied for use as top-coat and intermediate layers in a three or more layer environmental barrier coating system. Specifically, the room temperature Vickers-indentation-fracture-toughness testing and high-temperature stability reaction studies with Calcium Magnesium Alumino-Silicate (CMAS or "sand") are being conducted using advanced testing techniques such as high pressure burner rig tests as well as high heat flux laser tests .

Introduction

Advanced SiC/SiC ceramic matrix composites (CMCs) developed for gas turbine engine hot section component applications are susceptible to environmental attack from harsh combustion and general operation. This is why it is necessary to apply layers of environmental barrier coatings (EBCs) to protect SiC/SiC CMCs.

EBC materials have to withstand the extremely high temperature and corrosive environment, and integrate well with the CMCs to ensure excellent thermal cyclic durability. Advanced multi-component oxide and silicate composites are being developed to improve the coating mechanical integrity and environmental stability for CMCs.

SiC/SiC CMC gas turbine components generally require a layered environmental barrier coating system for improved performance, stability, and durability. EBCs are doped with rare earths and other metal oxides to improve their thermal mechanical and physical properties at high temperature. EBC top coats and intermediate coatings are typically made of rare-earth doped oxides and silicates. The coatings stability with calcium magnesium alumino-silicates (CMAS), which is sand and a common air born pollutant, is critical. The objective of this study is to determine the mechanical performance of several candidate EBC systems. The stability of candidate EBC material and coating systems in the presence of CMAS is also investigated.

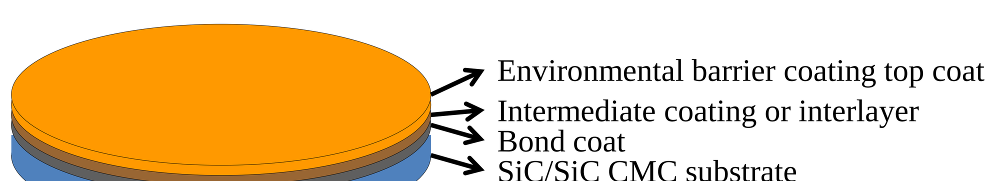
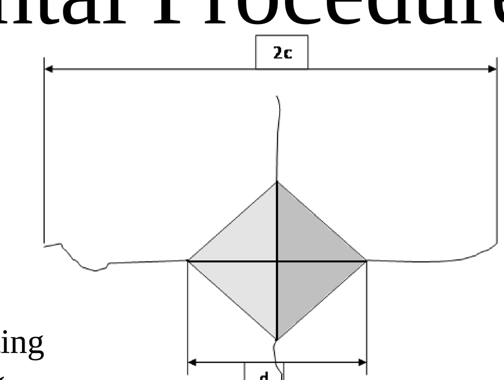


Figure 1: Shows a schematic of an EBC system with all 3 layers of coatings shown on SiC/SiC CMC substrate.

Experimental Procedure

- Sample preparation
  - Sintering
  - Polishing
- Indentation
- CMAS reaction
  - SEM EDS
  - X-ray diffraction
- Laser high heat flux testing
- High pressure burner rig



$$Kc = X\left(\frac{E}{H}\right)^{.5}\frac{P}{c^{1.5}}$$

$$HV = 1854.4\left(\frac{P}{d^2}\right)$$

EBC Materials Tested

- **Vickers Indentation Fracture Toughness**
  - Oxides
    - HfO_2
    - HfO_2+50wt%Si
    - HfO_2+5wt%Y_2O_3
    - ZrO_2 + 4.5wt%Yb_2O_3 + 4wt%Gd_2O_3 + 3.5wt%Y_2O_3 (ZrO 311)
  - Silicates
    - Barium Strontium Alumino-Silicate (BSAS)
    - $Al_6Si_2O_{13}$ (Mullite) + 20wt% BSAS
- **CMAS Reaction**
  - Oxides
    - HfO_2+5wt%Y_2O_3
    - HfO_2 + 50wt% (HfO_2+5wt%Y_2O_3)
    - HfO_2 + 50wt% (HfO_2+ 20wt%(Y, Gd, Yb)$_2O_3$)
    - ZrO_2 + 3.0wt%Y_2O_3 + 3.2wt%Gd_2O_3 + 3.7wt%Yb_2O_3 (ZrO 312)
    - ZrO_2 + 4.5wt%Yb_2O_3 + 4wt%Gd_2O_3 + 3.5wt%Y_2O_3 (ZrO 311)
  - Silicate
    - Yb_2SiO_5
    - $Al_6Si_2O_{13}$ (Mullite)
    - BSAS+25wt% (ZrO_2+14.3wt% (Y, Gd, Yb)$_2O_3$))
    - Er_2SiO_5
  - Hybrid Electron Beam Physical vapor Deposition (EB-PVD)– plasma coating system consisting of ZrO_2 and silicate system.

Sample Configurations

- 1in diameter x 1/8in thick disc specimens
- Hybrid Air EB-PVD coatings on CMC used for laser high heat flux tests

Hot press conditions
- Temperature = 1300 ˚C to 1700 ˚C
- Pressure = 69MPa to 103MPa
- Atmosphere = Vacuum

Results

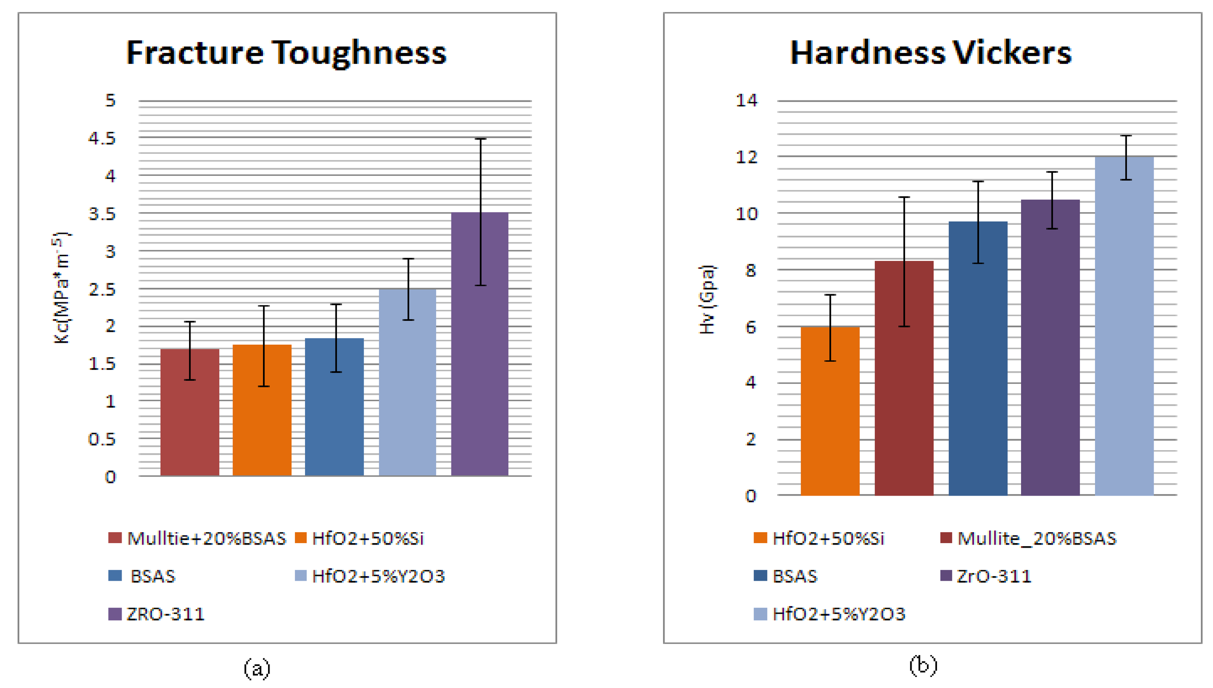
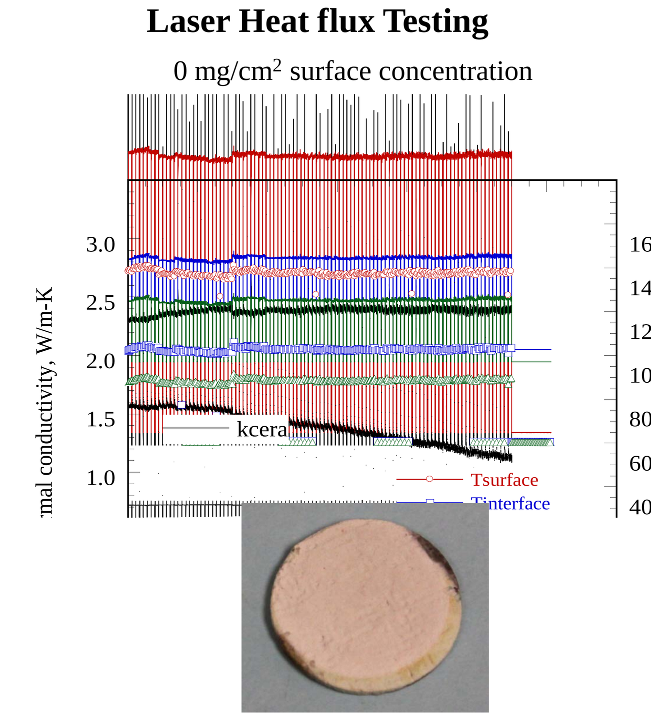


Figure 2: The initial vickers indentation results of non-CMAS-reacted coatings. (a) the mean value of each samples Kc was measured from the crack lengths. ZrO 311 was the toughest material. (b) the samples Hv as measured using the length of the diagonals. Hardness data was easily taken from the fracture toughness tests so (b) shows the hardest material as the HfO_2 + 5wt%Y_2O_3.

Laser Heat flux Testing



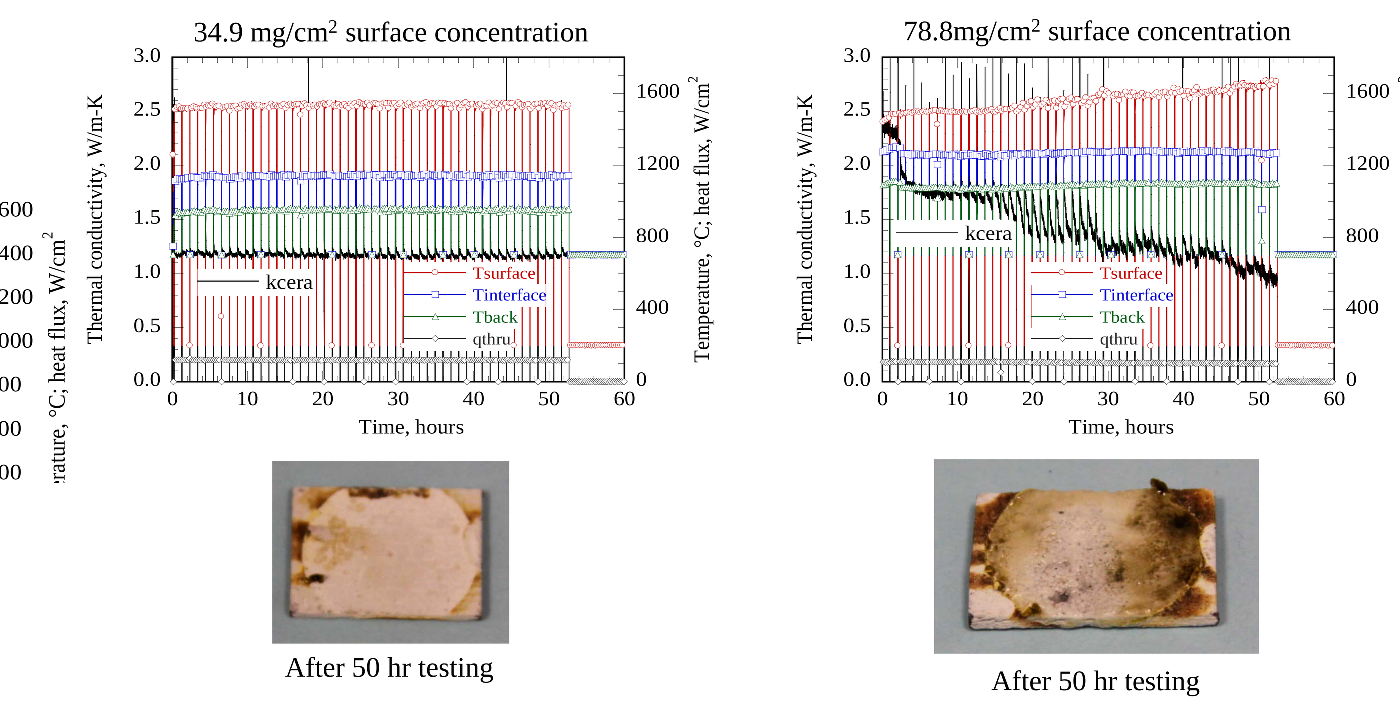


Figure 4: (above) Laser-high-heat flux tests were conducted on three structurally identical samples. With surface concentration increasing from left to right is evident that the CMAS is causing damage and melting of the coatings. (Left) the increase in conductivity is due to the continued sintering from the high temperatures.

Figure 4: (above) is a hybrid EB-PVD coating system that consists of multiple layers. The following list shows the layers of this system.
1. ZrO_2+(Y, Gd,Yb)$_2O_3$+TiO_2+Ta_2O_5
2. HfO_2+Al_2O_3+SiO_2+(Y, Gd,Yb)$_2O_3$
3. $Yb_2Si_2O_7$
4. $Yb_2Si_2O_7$ +20%BSAS
5. Si
6. SiC/SiC CMC

CMAS Reaction and Behavior With Coatings

- Recession
  - Melting
  - Evaporation
- Reaction and chemical change
- Penetration and void generation

Green: Hf
Yellow: Ca

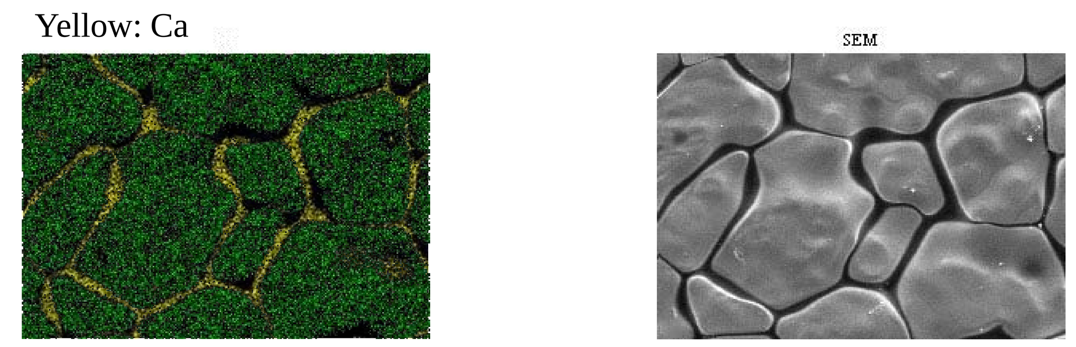


Figure 3 (above): SEM images that span ≈180µm Right, secondary electron image showing the topology of HfO_2 + 50wt% (HfO_2+ 20wt%(Y, Gd, Yb)$_2O_3$). Left, two EDS map images showing Hf (green) and Ca (yellow) locations. This image illustrates the effect of penetration of CMAS into the material.

High Pressure Burner Rig Test – Tyrannohex SA and Er2SiO5

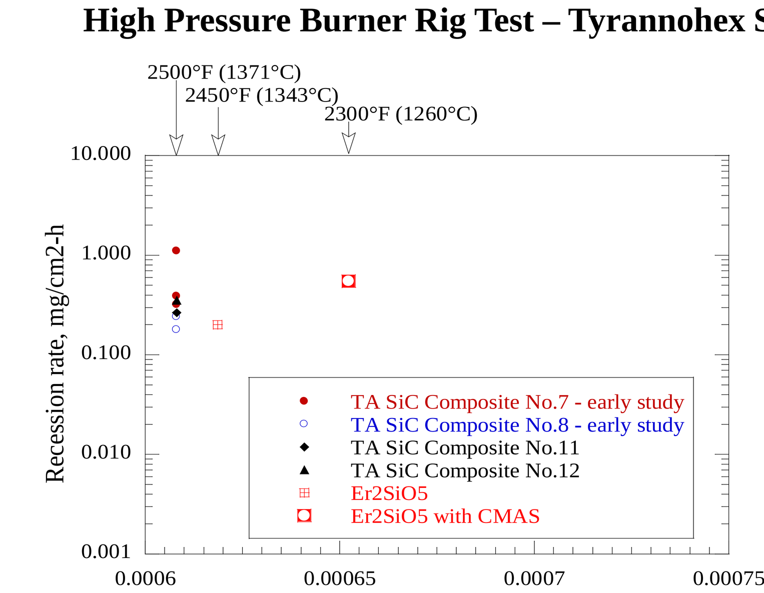
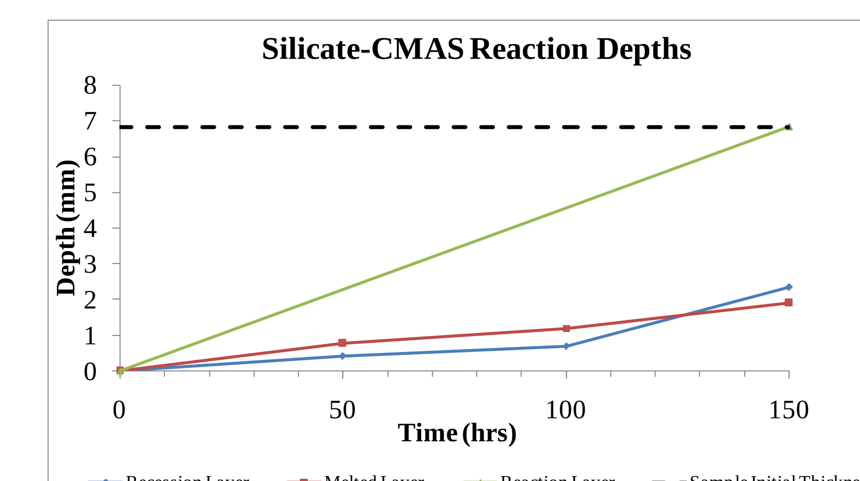


Figure 5: (above) Shows the recession of TA (Tyrannohex SA) SiC Composite as well as the recession of the Er_2SiO_5 in the high pressure burner rig (HBPR). It is shown that CMAS seemed to have a detrimental effect on the Er2SiO5 with a higher recession rate. The HBPR allows for gas turbine engine simulation testing at high pressure, temperature, and gas velocity.

Figure 6: (right) Shows the increasing thickness of various layers of mullite. Each layer represents a different effect CMAS had. Time in hours is on the x axis. Depth is on the y.



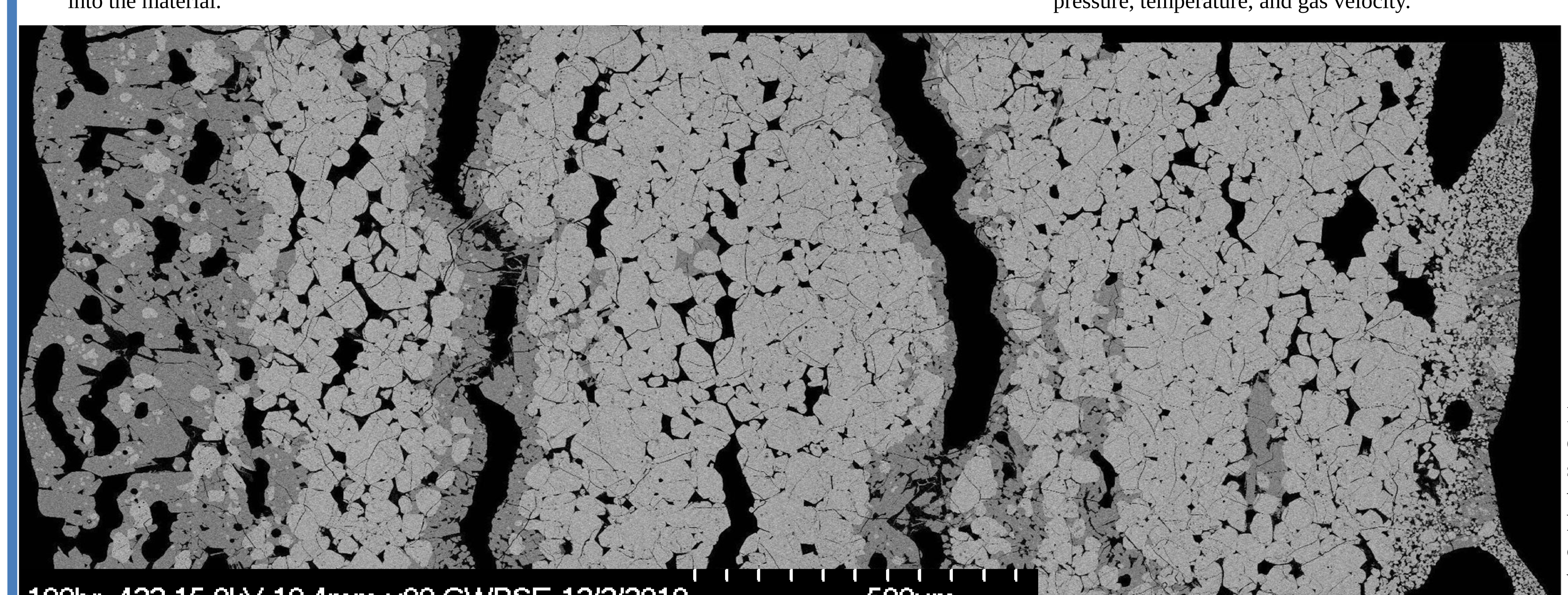


Figure 7 (left): SEM backscatter electron image with three images stitched together. Yb_2SiO_5 exposed to CMAS twice for a total of 100 hr. This photo illustrates the combined effects of penetration, void generation, reaction/chemical change, and melting.

Concluding Remarks

Initial fracture toughness testing using the Vickers indentation approach has shown that the ZrO_2 and HfO_2 coating materials are the most fracture resistant. Further testing is being considered to determine the strength and fracture toughness of materials reacted with CMAS.

Seven mechanisms of CMAS interactions with the coating materials have been identified. While the oxides were more stable than the silicates, they were still affected by penetration and void generation from CMAS especially when initial high porosity is present. Silicates reacted strongly with the CMAS generally decreasing the melting point and causing the coating to change phases as evidenced from x-ray diffraction such as in Yb_2SiO_5 case. Some coating materials experienced combinations of all of the effects. The laser-high-heat flux tests showed the damage and potentially reduced temperature capability caused by the CMAS on a multilayer hybrid EB-PVD/Plasma Spray oxide-silicate EBC. This can be fatal to the coating structure as the operating temperature approaches the melting point of these materials after reacting with CMAS. The HPBR tests showed that the CMAS-reacted Er_2SiO_5 seemed to be damaged (delamination and disintegration) and had higher recession rates compared to the non-reacted Er_2SiO_5.

While these studies are not complete, the current results easily showed that CMAS can cause serious damage to the coating or coating materials. Coating that have improved resistance to CMAS must be designed and tested for advanced EBC systems.

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